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SILICON SUBSTRATE PREPARATION FOR EPITAXIAL DIAMOND CRYSTALS.

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Abstract

Using the microwave plasma assisted chemical vapor deposition technique (MPCVD), we study the role of the (100) silicon substrate preparation prior to the Ultra Short Bias Enhanced Nucleation (USBEN) step via various pretreatments. We study the effect of the silicon HF cleaning coupled with the hydrogen plasma exposure in order to determine the efficiency of these pretreatments to eliminate the native oxide layer on the silicon surface prior to the bias step. We show that the residual oxygen content in the gas phase during the hydrogen plasma exposure can strongly affect the nucleation density because of the formation of an oxide layer which is detrimental for the synthesis of Highly Oriented Diamond (HOD) films. Moreover, we study the effect of the carburation step, often used for the synthesis of HOD films, and show that it raises the percentage of epitaxial crystals and the crystal density. Thus, we show that the achievement of high epitaxial crystal density is not only due to the BEN parameters but also to the silicon substrate preparation. As a conclusion, it appears that the silicon substrate preparation prior to BEN is fundamental for controlling the quality of epitaxial diamond films.

Introduction

The synthesis of diamond films by chemical vapor deposition on non-diamond substrates is attractive for numerous electronic or optical applications because of extreme diamond properties. However, many of them are limited by the formation of chemical and structural defects. Also, the synthesis of monocrystalline diamond films represents a considerable stake for this type of applications. The Bias Enhanced Nucleation (BEN) pretreatment presented by Yugo et al.[1], Jiang et al.[2] and Stoner et al.[3] allows the synthesis of Highly Oriented Diamond (HOD) films on (100) single silicon crystal. This one is the most used substrate for the synthesis of HOD films because it is cheap, available in large size and the proof has been made that it is possible to obtain epitaxial relations between diamond and silicon[4]. The BEN step leads to a high nucleation density increasing with a variable percentage of epitaxial crystals. HOD films are formed by growth under conditions which promote <100> texture from both epitaxial and randomly oriented diamond crystals. These last ones are progressively eliminated during the thickening[5]. As a consequence, the structure of HOD films depends on the altitude considered within the thickness of the deposit. For a thick film, the structure at the surface is close to a single crystal but the bulk structure is not monocrystalline because of the presence of grain boundaries and misoriented crystals. If all the crystals were epitaxial and the crystal density sufficient to form a film, it would be possible to obtain a very thin monocrystalline diamond film on single silicon substrate. Several studies focus their works on the BEN step and try to identify the diamond nucleation mechanisms but the problem is very difficult to solve because the interactions between the substrate and the plasma are complex to characterize. So, very different models have been developed to explain the mechanisms of bias enhanced epitaxial nucleation[6-11], and today a complete explanation is still under investigation.

The low epitaxial ratio is a real stake for improving the HOD films quality[12]. The epitaxial ratio is defined as the number of epitaxial crystals divided by the number of total crystals. In this study we focus our attention on the first stage of the nucleation by characterizing the epitaxial ratio and the crystal density after a short growth step. The question arises as to whether values of epitaxial ratio and crystal density are limited by the BEN step or/and by the previous steps, which also modify the silicon surface. The aim of these steps is to clean the

silicon surface. Indeed, in the case of silicon substrates, hydrocarboneous molecules and native oxide layer are the major contaminants that need to be eliminated in order to get a clean surface. The hydrocarboneous contaminations are often eliminated *ex situ* by a degreasing of the surface with acetone and/or simmered trichloromethane[3,13]. This procedure, generally used for diamond synthesis, is very simple compared to those developed for the microelectronic (RCA cleaning method[14,15]). So, in our case the surface quality is lower than the surface quality reached with the RCA cleaning method. Concerning the native oxide layer which has a typical thickness of 1.5 nm[16], it is now well established that etching of the silicon surface in concentrated or dilute hydrofluoric acid solutions removes any oxide layer and produces stable, hydrogen-terminated surfaces [13,17,18]. After the chemical preparation of the substrate, it is loaded into the reactor and the first step is, after pumping in the chamber, to etch *in situ* the substrate in a hydrogen microwave plasma. This step is frequently named by the authors the etching step. It lasts between 10 and 30 minutes according to the authors. The hydrogen plasma exposure has two purposes: raising and stabilizing the temperature of the substrate and removing the native oxide layer[7-9,13,19]. The first one is necessary because the nucleation by substrate biasing is very poor at low temperature but the second one is less obvious. This is because the reduction of SiO₂ in the hydrogen plasma could be counterbalanced by the oxidation from the residual oxygen present in classical reactors used for diamond synthesis[20] which are not UHV system. In our case, before the hydrogen plasma exposure, we heat the substrate via a heating substrate holder[21] to reduce the duration of the hydrogen plasma exposure and to study the effects of the plasma exposure duration on the silicon surface independently of the temperature. To evaluate the effects of the previous steps, we keep constant the bias and growth parameters. If the bias step was too long, it could hidden the effects of the previous ones. In order to avoid this, we use the Ultra Short Bias Enhanced Nucleation step (USBEN) developed in another paper[21].

Experimental set up.

The experiments have been carried out in a 2.45 GHz microwave plasma reactor with a 1.5kW Astex source which has been described in detail earlier[22]. The geometry of the cavity has been modified in order to have homogeneous and reproducible deposits as reported in a previous study[12]. These conditions are essential to correlate macroscopic parameters of the process to microscopic characteristics of the deposit related to epitaxial nucleation mechanisms. The result of various optimisations in terms of cavity geometry design,

behaviour of the bias plasma and choice of experimental parameters allows the bias time to be drastically reduced: it is the USBEN step. The substrate used is a mirror-polished (100) oriented silicon wafer (square of $10 \times 10 \text{ mm}^2$). We use high purity hydrogen ($\text{O}_2 < 5 \text{ ppm}$) and methane ($\text{O}_2 < 3 \text{ ppm}$) gases. The cavity can be pumped down to 10^{-7} hPa by means of a turbomolecular pump prior to the synthesis.

Results and discussions.

-USBEN synthesis and characterization of the deposit.

Experimental conditions of standard USBEN synthesis are reported in table 1. The silicon substrate is cleaned in acetone, simmered in trichloromethane and chemical etched in 40% hydrofluoric acid for 10 seconds just before the synthesis. When the sample has been submitted to a 20 minutes growth step after biasing, we obtained isolated crystals (fig. 1). So, we perform quantitative characterization of the deposit using a scanning electron microscopy (SEM Philips XL30S-FEG) coupled with an image analysis software (Aphelion, ADCIS S.A.) to calculate the crystal density and the epitaxial ratio. For experimental conditions defined in table 1, the crystal density is equal to $4.7 \cdot 10^9 \text{ cm}^{-2}$ and the epitaxial ratio is equal to 6%. The epitaxial ratio is determined by counting more than 300 particles for statistical precision. The analysis is local but as the deposit is homogeneous, it is representative of the whole surface of the sample. The low epitaxial ratio is nevertheless sufficient to obtain a HOD film after 10 hours of growth because the epitaxial crystal density associated is high enough ($2.8 \cdot 10^8 \text{ cm}^{-2}$) (fig. 2).

Ex situ preparation of the silicon substrate.

The HF cleaning of the silicon surface is frequently used for the synthesis of HOD films[23-30]. However, the HF-etched Si(100) surfaces are terminated by different hydride species which are arranged in a disordered manner, causing a very rough surface[31]. The hydrogen-terminated silicon surface has the property to be hydrophobic contrary to the oxidised silicon surface which is hydrophilic. In order to study the influence of the HF pretreatment, we performed two syntheses with and without HF cleaning of the surface. Experimental conditions are those of the standard experiment (table 1). With the HF cleaning the crystal density is equal to $4.7 \cdot 10^9 \text{ cm}^{-2}$ whereas without this one, the crystal density is equal to $3.8 \cdot 10^9 \text{ cm}^{-2}$. We note that the nucleation density is quite the same for both experiments which means that, in our case, the HF preparation does not influence strongly the crystal density. One can ask if the heating step does not induce the formation of an oxide layer which could explain the

low variation of crystal density. The state of a silicon surface can most easily be checked by a water drop test. On a hydrophobic surface the water drop keeps ball-shaped whereas on a hydrophilic surface it flows into a flat form. After the HF cleaning, the silicon surface is hydrophobic that confirms the absence of an oxide layer. Just after the heating step, we stopped the experiment and done the water drop test. The surface was hydrophilic like a sample not HF cleaned. As a consequence, heating the substrate under a hydrogen flow with residual oxygen ($O_2 < 10$ ppm) leads to the formation of an oxide layer because the Si(001) passivated surface does not remained stable during the heating. So, in our case, the HF cleaning is useless and the question is to know if the exposition of the oxidised surface to a hydrogen plasma remove this oxide layer.

-In situ preparation of the silicon surface.

It is not possible to calculate from thermodynamic considerations the transition line from oxidation to reduction of SiO_2 by hydrogen because the considered system is not at the thermodynamic equilibrium. *In situ* surface analysis are difficult to perform because of the presence of the plasma and the moderate pressure (10-30 hPa) used. The stopping of the microwave plasma studying the surface at lower pressure does not seem to be a solution because if the surface was cleaned during the hydrogen plasma exposure, it will be instantaneously oxidised by the residual oxygen just after stopping the microwave plasma. In this context, we study the influence of residual oxygen by introducing small quantities of oxygen into the gas phase during the hydrogen plasma exposure step only via an adjustable leak valve previously calibrated. As it is agreed by most authors that the presence of an oxide layer inhibits the nucleation process[32,33], we measure the crystal density after the USBEN step for various contents of oxygen in the gas phase during the hydrogen plasma exposure. For these experiments, we used experimental conditions reported in table 1 except for the hydrogen plasma exposure where we added oxygen. Figure 3 shows the evolution of crystal density according to the oxygen contents. We can observe that for oxygen contents lower than 20 ppm, the crystal density is constant and equal to roughly 2.10^9 cm⁻². For values comprised between 20 and 100 ppm, the crystal density drops quickly and for higher values (>100 ppm) the crystal density is equal to zero. This curve gives us an information about the transition from reduction to oxidation of the silicon surface. For values lower than 20 ppm, the hydrogen plasma etches the SiO_2 layer and the crystal density is very high. If the oxygen content in the gas phase exceeds 100 ppm, the exposition of the surface to the plasma induced an oxidation of the silicon which prevents diamond nucleation. The intermediate crystal

density values probably correspond to a moderate oxidation of the silicon surface followed by an etching of the formed SiO₂ layer during the USBEN step. So the efficiency of the USBEN step is reduced and the associated crystal density is intermediate. Thus, we show that the reduction of the SiO₂ by hydrogen is efficient only if the gas phase does not contain too much oxygen. Otherwise, the surface is oxidised during the hydrogen plasma exposure and the efficiency of the bias step in terms of nucleation is strongly reduced. If we do not perform the heating step and use a longer hydrogen plasma exposure to reach a sufficiently high temperature for the bias step, the HF cleaning could be useless if the residual oxygen is too high. In fact the *ex situ* HF passivation could be avoided if the *in situ* reduction step is well controlled. The critical value between the reduction and the oxidation step is not an absolute value; it is likely to depend on the substrate temperature, the pressure and the microwave power.

In order to determine the minimum duration of the hydrogen plasma exposure, we performed several experiments associated with different exposure durations. We noted, that for each experiment, the substrate temperature during the hydrogen plasma exposure was kept equal to 1073 K, whatever the duration is, thanks to the substrate heater. In our case, the minimum time defined was roughly 1 to 3 minutes. This short etching step avoids strong surface roughness modifications which may affect the nucleation density.

-Influence of the hydrogen / methane plasma exposure.

The hydrogen / methane plasma exposure prior to the bias step is often named "carburation" step by the authors. This step is actually very controversial because it has been demonstrated that diamond epitaxy can be achieved without this one [7,8,34-39]. In order to study the influence of this step, we performed two experiments with and without hydrogen / methane plasma exposure and characterized them in terms of epitaxial ratio and crystal density after 20 min of growth. Experimental conditions and results of these experiments are reported in table 2. This step increases strongly the crystal density and the epitaxial ratio. We obtained 16% of epitaxial crystals for a total crystal density equal to $5.1 \cdot 10^9 \text{ cm}^{-2}$ with only 20s of bias step. So the modification of the silicon surface before the bias step has a major effect. It could be a solution to raise the epitaxial ratio to higher values finding the conditions which promote epitaxy by modifying the silicon surface prior to the USBEN.

Conclusion.

The synthesis of HOD films is very sensitive to the silicon surface state just before the biasing step. The hydrogen passivation of the silicon by HF acid is not a crucial step for eliminating the SiO₂ layer because of the subsequent hydrogen plasma exposure. In fact, we show that, according to the residual content of oxygen in the gas phase during the hydrogen plasma exposure, there are two possibilities: oxidation of the silicon or reduction of SiO₂. We determine the critical oxygen content during the hydrogen plasma exposure using a very short biasing step followed by a short growth step and calculating the crystal density knowing that it is poor on SiO₂. Up to now, the base vacuum chamber for CVD diamond synthesis is not very low[40]. Therefore, improvements of the base vacuum in the growth chamber are useful to prevent silicon oxidation and favour SiO₂ reduction by hydrogen plasma. Nevertheless UHV (10⁻⁸-10⁻¹¹ hPa) conditions are not necessary, as we shown, to avoid silicon oxidation. In these conditions, we have an epitaxial ratio of 6% for a crystal density of 4.7 10⁹ cm⁻² using an USBEN step of 30s. We also show that it is possible to change the epitaxial ratio modifying the step before the bias step. Exposing the silicon surface to a methane-hydrogen plasma before the USBEN step leads to an epitaxial ratio of 16% for a crystal density of 5 10⁹ cm⁻² for only 20s of biasing. So it appears possible to change the epitaxial quality of the diamond deposit controlling the steps before the bias.

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	Heating	H ₂ plasma	Bias	Growth
Time	5 min	3 min	30 s	20 min/10 h
Total Pressure (hPa)	13	13	13	13 / 27
Microwave power (W)	-	300	300	300 / 270
Total Flow rate (sccm)	400	400	400	150
Gas composition (Vol %)	100 % H ₂	100 % H ₂	4 % CH ₄ in H ₂	1 % CH ₄ in H ₂
O ₂ content (ppm)	<10	<10	<10	<10
Bias voltage (V)	0	0	-150	0
Temperature (K)	813	1073	1113	1073
Substrate	Silicon (100) square of 10 * 10 mm ²			
Substrate-holder	Molybdenum			
Electrode	Graphite $\phi = 30\text{mm}$			

Table 1

	Heating	H₂ / CH₄	Bias	Growth
		or H ₂ exposure		
Time	5 min	10 min / 3 min	20 s	20 min
Total Pressure (hPa)	13	13 / 13	13	13
Microwave power (W)	-	300 / 300	300	300
Total Flow rate (sccm)	400	400 / 400	400	150
Gas composition (Vol %)	100 % H ₂	4 % CH₄ in H ₂ / 100% H ₂	4 % CH ₄ in H ₂	1 % CH ₄ in H ₂
O ₂ content (ppm)	<10	<10	<10	<10
Bias voltage (V)	0	0	-150	0
Temperature (K)	813	1073 / 1073	1113	1073
R E S U L T S				
	Epitaxial ratio		Crystal density	
H₂ / CH₄ 10':	16%		5.1 10⁹ cm⁻²	
H ₂ 3':	6%		6.6 10 ⁸ cm ⁻²	

Table 2

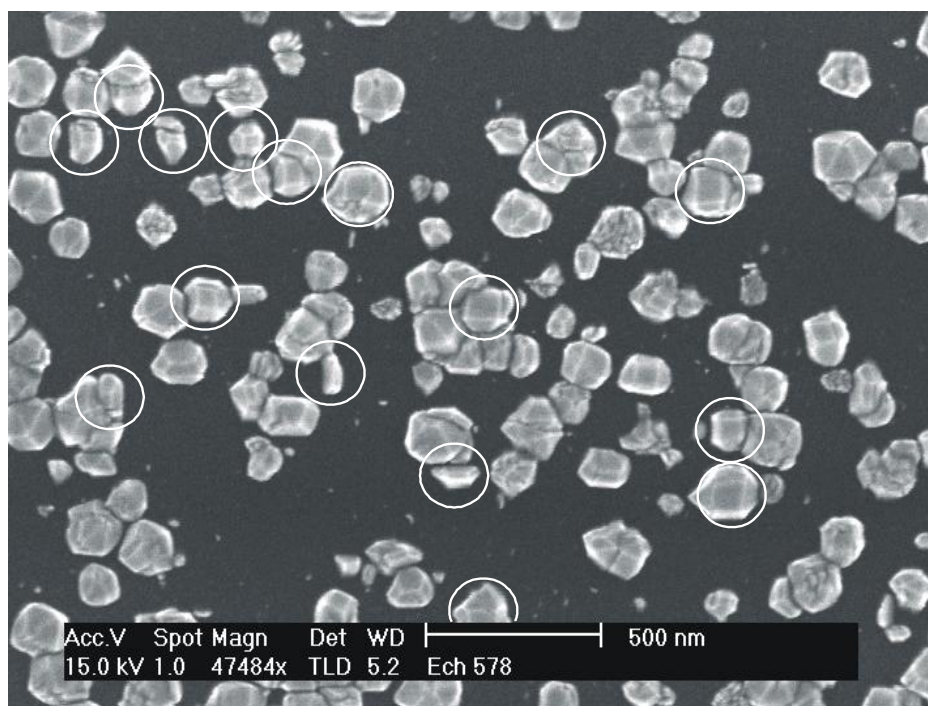


Figure 1

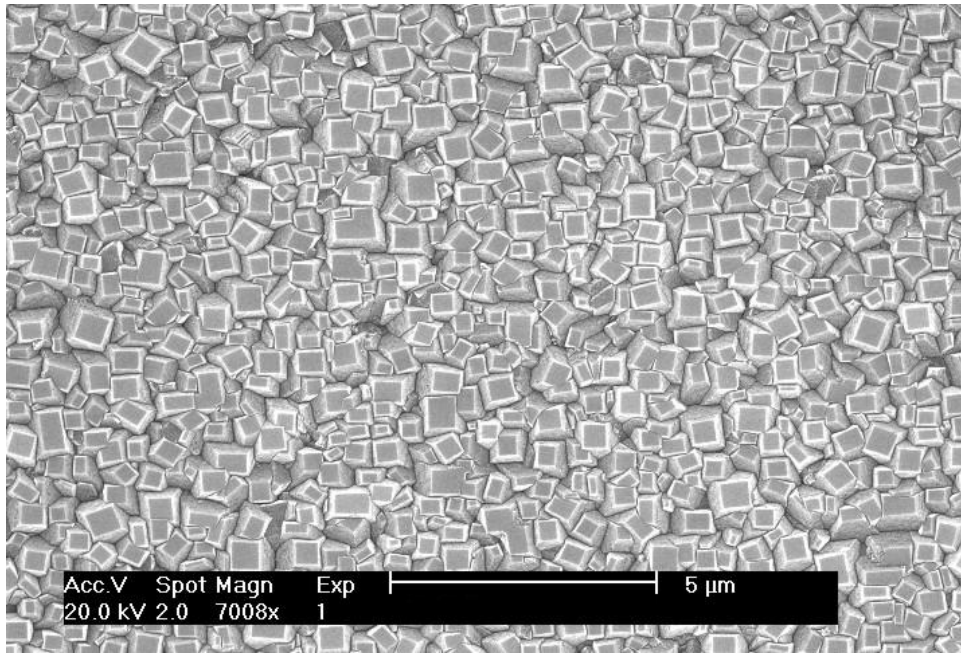


Figure 2

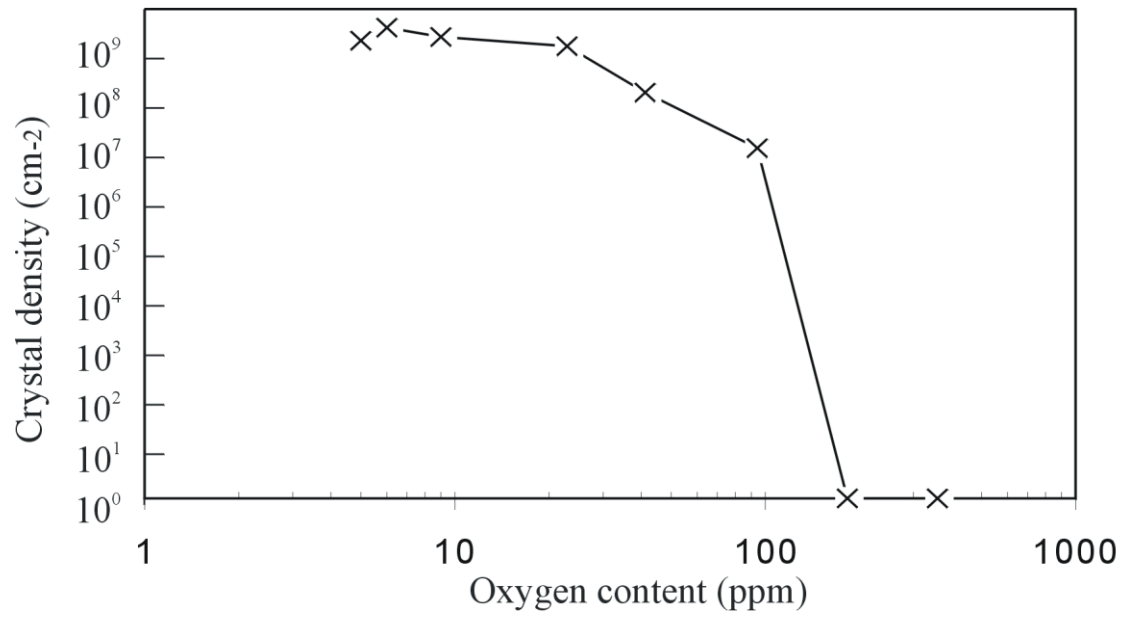


Figure 3

Figure Captions

Table 1

Experimental parameters used for the deposition of oriented diamond crystals using the USBEN step.

Table 2

Experimental parameters used for the deposition of oriented diamond crystals using the USBEN step after 3 minutes to a hydrogen plasma or 10 minutes to a hydrogen-methane plasma.

Figure 1

Scanning electron microscopy micrograph of diamond deposits obtained by USBEN (see table 1) step followed by 20 min of growth step where white circles point out some epitaxial crystals.

Figure 2

Scanning electron microscopy micrograph of diamond deposits obtained by USBEN step followed by 10 hours of growth step (see table 1).

Figure 3

Evolution of crystal density obtained by USBEN (table 1) according to the oxygen contents in the gas phase during the hydrogen plasma exposure.